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Chromium speciation in environmental samples using a solid phase spectrophotometric method

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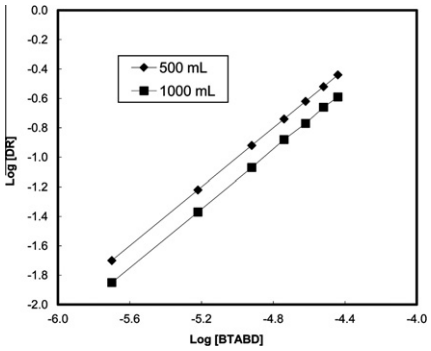
HIGHLIGHTS

- Chromium can be determined efficiently with BTABD using SPS.
- The proposed method has several advantages to warrant its use.
- The proposed method has been applied to determine chromium in natural waters.
- The proposed method is simple and more sensitive than other methods commonly used at microgram level.

GRAPHICAL ABSTRACT

The log–log plot of the distribution ratio vs. BTABD concentration; conditions, pH 7.5, 0.6 mg L^{-1} Cr(III), 75 mg Sephadex DEAE A-25, stirring time 20 and 30 min for 500 and 1000 ml samples, respectively.



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ABSTRACT

A solid phase extraction technique is proposed for preconcentration and speciation of chromium in natural waters using spectrophotometric analysis. The procedure is based on sorption of chromium(III) as 4-(2-benzothiazolylazo)2,2′-biphenyldiol complex on dextran-type anion-exchange gel (Sephadex DEAE A-25). After reduction of Cr(VI) by 0.5 ml of 96% concentrated H_2SO_4 and ethanol, the system was applied to the total chromium. The concentration of Cr(VI) was calculated as the difference between the total Cr and the Cr(III) content. The influences of some analytical parameters such as: pH of the aqueous solution, amounts of 4-(2-benzothiazolylazo)2,2′-biphenyldiol (BTABD), and sample volumes were investigated. The absorbance of the gel, at 628 and 750 nm, packed in a 1.0 mm cell, is measured directly. The molar absorptivities were found to be 2.11×10^7 and 3.90×10^7 L mol^{-1} cm^{-1} for 500 and 1000 ml, respectively. Calibration is linear over the range 0.05–1.45 μg L^{-1} with RSD of <1.85% ($n = 8.0$). Using 35 mg exchanger, the detection and quantification limits were 13 and 44 ng L^{-1} for 500 ml sample, whereas for 1000 ml sample were 8.0 and 27 ng L^{-1}, respectively. Increasing the sample volume can enhance the sensitivity. No considerable interferences have been observed from other investigated anions and cations on the chromium speciation. The proposed method was applied to the speciation of chromium in natural waters and total chromium preconcentration in microwave digested tobacco, coffee, tea, and soil samples. The results were simultaneously compared with those obtained using an ET AAS method, whereby the validity of the method has been tested.

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Introduction

Speciation information of heavy metal ions is very important for their toxicity and biological role of a particular element vary greatly depending on its chemical form [1,2]. Speciation studies of heavy metal ions are generally focused on chromium, arsenic, antimony, etc. The toxicity of chromium depends on the chemical properties and bioavailability of the species, which are related to their characteristics and concentrations [2].

Chromium(III) is known to be an essential trace nutrient involved in the mechanism of the action of the pancreatic hormone insulin and/or glucose metabolism [3]. On the other hand, Cr(VI) is toxic for biological systems especially for human. Chromium(VI) is water soluble and extremely irritating and toxic to human body tissue owing to its oxidizing potential and permeability of biological membranes [4]. The major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and local effects in lungs [5]. Owing to the high oxidation potential and the ease penetration from biological membranes, Cr(VI) compounds are approximately 100 times more toxic than Cr(III) salts [6,7]. The US EPA has set the concentration of 0.01 mg L^{-1} of total chromium for drinking water as "maximum contaminant level goals". World Health Organization states that the guideline values of Cr(VI) is 50 μg L^{-1} [8]. Due to these factors, accurate and facile determinations of both valence forms in environmental samples take an important role in analytical chemistry.

Direct determination of the chromium species including Cr(III) and Cr(VI) by instrumental techniques including atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), etc. is not suitable [9,10]. Separation–preconcentration techniques including solvent extraction, cloud point extraction and solid phase extraction [11,12] have been used for speciation of Cr(III) and Cr(VI). Also by using the separation and preconcentration techniques, the detection limit for chromium is improved.

Solid-phase spectrophotometry (SPS) is a technique based on the preconcentration of the substance in question on a solid, aided by complexing (or other reagents), and the subsequent measurement of the absorbance of the species in the solid phase. This provides SPS with an increase in selectivity and sensitivity over other methods [13–17]. In this work, a dextran-type exchanger, i.e. a mixed ligand complex is used as the basis of a method to determine chromium with BTABD as complexing agent.

Experimental

Apparatus

Absorption spectra and absorbance measurements were recorded and measured using a Perkin-Elmer λ3B double beam UV–VIS spectrophotometer and 1.0 mm quartz cuvettes. Furthermore, an Agitaser 2000 rotating bottles agitator (Tecnotrans, Barcelona, Spain), a desk centrifuge (URA Technic 2610, Barcelona, Spain) were used. An Orion research model 601A/digital ionalyzer fitted with a combined glass–calomel electrode was used for pH adjustment and checking the pH value of buffer solutions. A Perkin Elmer atomic absorption spectrometry model *A Analyst* 300 was used for all ET AAS measurements.

Reagents

All chemicals used were of analytical-reagent grade unless stated otherwise. Doubly distilled water was used and all experiments were carried out at room temperature.

4-(2-Benzothiazolylazo)2,2′-biphenyldiol was synthesized according to the method described previously [18,19]. Stock solution of 3×10^{-3} M was prepared by dissolving an appropriate weight of the pure reagent in least amount of ethanol (15 ml) and then diluted to the mark in a 100-ml measuring flask with ethanol.

Chromium(VI) and chromium(III) working standard solutions were all prepared by appropriate dilution of, respectively, 1000 mg L^{-1} $K_2Cr_2O_7$ (Merck, Darmstadt, Germany) and 1000 mg L^{-1} $CrCl_3{\cdot}6H_2O$ (Sigma, St. Loius, MO, USA) stock solutions. The reduction of Cr(VI) to Cr(III) was performed by the addition of 0.5 ml of concentrated H_2SO_4 (Merck, Darmstadt, Germany) and 0.5 ml of ethanol (Merck) to the test solution [6].

Solid ion exchanger

Sephadex DEAE A-25 and Sephadex QAE A-25 anion exchangers (Pharmacia Fine chemicals) (Sigma, St. Loius, MO, USA) were used in the chloride form in the original dry state as obtained from the supplier and without pre-treatment in order to avoid contamination.

Buffer solutions

Thiel buffer solutions of different pH's from 2.0 to 12 were prepared as described early [20].

Absorbance measurements

The absorbance of the reaction product sorbed on the exchanger was measured in a 1.0 mm cell at 628 and 750 nm (the latter is within the range where only the exchanger absorbs light against a 1.0 mm cell packed with exchanger, which has been equilibrated with the blank solution). The net absorbance, A_{RP}, for the complex was obtained from [21]:

$A_{RP} = A_{628} - A_{750}$.

General procedure

- To a 1000 ml water sample containing either 0.05–1.45 or 0.03–0.70 μg L^{-1} of Cr(III), 6.0 ml of 3×10^{-3} M BTABD solution, and 100 ml of thiel buffer of pH 7.5 were added. The solution was transferred to a 2000 ml polyethylene bottle and 75 or 35 mg, respectively, of the Sephadex DEAE A-25 anion exchanger was added. The mixture was shaken mechanically (rotator) for 30 min. The colored exchanger beads was then collected by filtration under suction and, with the aid of a pipette, was packed into a 1.0 mm cell together with a small portion of the filtrate. The cell content was centrifuged for 1.0 min at 2500 rpm. A blank solution containing all of the reagents except the analyte was prepared in the same way as described for the sample. The absorbance of the sample at 628 and 750 nm was measured against a reference cell, similarly packed with exchanger equilibrated with the blank solution and the net absorbance A_{RP} was obtained as described under absorbance measurements.
- For 500 ml samples, solutions containing 0.1–4.0 or 0.05–2.5 μg L^{-1} of Cr(III), same concentration of reagent, and buffer of pH 7.5 used above for 1000 ml and 75 or 35 mg of the Sephadex DEAE A-25 anion exchanger were added. The mixture was shaken mechanically using (rotator) mechanical for 20 min. As mentioned previously, the absorbance of the colored species was measured at λ_{max} 628 and 750 nm as with the above procedure.

Analysis of the real samples

The water samples analyzed were collected in pre-washed (with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water, respectively) polyethylene

bottles. The samples were filtered through a Millipore cellulose membrane of pore size 0.45 μm. The samples were stored in 1.0 L polyethylene bottles and acidified to 1.0% with nitric acid and were subsequently stored at 4.0 °C in a refrigerator. In order to eliminate the chlorine in tap water, the samples were treated for 5.0 min with 5.0 g of activated charcoal and filtered before being transferred into a polyethylene bottle. Before the analysis, the pHs of the samples were adjusted to 7.5.

Prior to preconcentration step of the solid samples analyzed, tobacco, coffee, tea, and soil sample from Benha City were also microwave digested. Digestion conditions for microwave system for the samples were applied as 2.0 min for 250 W, 2.0 min for 0 W, 6.0 min for 250 W, 5.0 min for 400 W, 8.0 min for 550 W, vent: 8 min, respectively [22,23].

Tobacco, coffee and tea samples (1.0 g) were digested with 6.0 ml of HNO_3 (65%), 2.0 ml of H_2O_2 (30%) in microwave digestion system and diluted to 50 ml with deionized water. Soil sample (1.0 g) was digested with 6.0 ml of HCl (37%), 2.0 ml HNO_3 (65%) in microwave digestion system and diluted to 50 ml with deionized water. After microwave digestion, the volume of the sample was made up to 25 ml with distilled water. Blank was prepared in the same way as the sample, but omitting the sample.

Procedure for determination of Cr(VI) by ET AAS

To the real sample solutions one drop of H_2SO_4 and one drop of 0.01% $KMnO_4$ solutions were added and heated gently (5.0 min) for the oxidation of Cr(III) to Cr(VI). After cooling, one drop of 2.0 M HCl was added to destroy the excess of permanganate [24]. After oxidation, the sample was used for the analysis of Cr(VI) by ET AAS and absorbance was measured at 357.9 nm. The amount of Cr(VI) can be calculated from the calibrated plot which was drawn by taking the standard Cr(VI) solution.

Results and discussion

Absorption spectra

In solution, BTABD showed maximum absorbance at 517 (pH 7.5) and 482 nm (pH 3.5). It reacts with chromium(III) at pH values 7.5, to form a pink complex having a maximum absorbance at 573 nm. At pH 7.5, BTABD gives a yellow orange color when fixed on the Sephadex anion exchangers with an absorption maximum at 497 nm. The formed complex as a result of a reaction between Cr(III) and BTABD can be sorbed onto Sephadex anion exchangers. When sorbed, the complex shows a violet color with a high absorption band at λ_{max} 623 nm was obtained on using Sephadex QAE A-25. When Sephadex DEAE A-25 anion exchanger is used, a hyperchromic effect is observed and a bathochromic shift of the absorption maximum (628 nm) is obtained. Thus, this complex has obviously an anionic nature (due to the formation of 1:1 [BTABD to Cr(III)] ratio in the sorbed species) and it does not fix onto cation exchangers.

Optimization of conditions

Effect of pH

Various buffer media were used, viz. acetate, borate, phosphate, thiel and universal buffers [20] of different pH values. Thiel buffer solutions gave a suitable and stable color product that was suitable for all spectral measurements. The optimum pH for the formation and fixation of the complex falls in the range 6.5–8.5 (Fig. 1). At pH values of below 3.5, the complex is not fixed on the exchanger and at pH values of above 9.0, the net absorbance decreases due to an increase in the absorbance of the blank. The best of the buffer systems examined was boric acid–succinic acid, sulfate and tetraborate (pH 7.5). Moreover the optimum volume of pH 7.5 was found to be 100 mL, since the results were highly concordant at this volume.

Effect of reagent concentration

The influence of BTABD concentration on the absorbance of the complex was investigated. The net absorbance increased with BTABD concentration and the optimum values were obtained for concentrations of BTABD between 1.6×10^{-5} and 2.0×10^{-5} M for 1000 ml sample. An increase in BTABD concentration (Fig. 2) causes an increase in the absorbance of the blank. Hence, 1.8×10^{-5} M was selected for the standard procedures, since the results were highly concordant at this level of concentration.

Effect other experimental conditions

The optimum stirring time was 20 min for a 500 ml sample system and 30 min for a 1000 ml sample system (Fig. 3). The fixed species are stable for at least 6.0 h after equilibration. Examination of the solvent effects showed that solvent does not affect the reaction. Increasing the ethanol percentage has no effect on the absorbance of the formed complex. Using different ionic strength (μ), the absorbance of the complex matrix is not altered indicating that the complexation process is ionic strength independently. Reproducibility of the method is improved if the cells packed with the solid phase are centrifuged before spectrophotometric measurements are taken. The centrifugation time used here was 1.0 min at 2500 rpm. An increase in the amount of exchanger reduced the concentration of the species sorbed and hence the absorbance, whereas too small amount can result in operational difficulties. An amount of exchanger between 20 and 100 mg allows adequate working conditions. On the other hand, the use of different amounts, within the preceding range, permits the development of methods with different sensitivities. For all measurements, unless stated otherwise, 35 and 75 mg of exchanger was used as a compromise between maximum sensitivity and ease of operation. The most favorable sequence is "Cr(III)–BTABD-buffer" for the highest absorbance and the least time for maximum color development. All other sequences needed longer times and gave lower absorbance values.

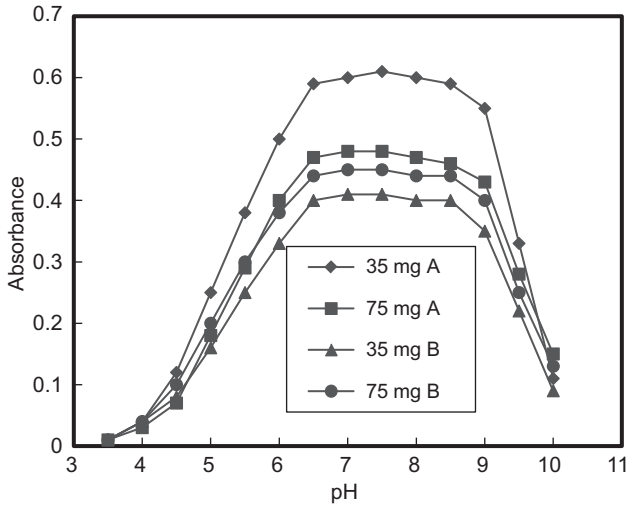

Fig. 1. Effect of pH on the fixation and complexation of (A) 1.5 μg L^{-1} Cr(III) for 500 ml, and (B) 0.6 μg L^{-1} Cr(III) for 1000 ml using 35 and 75 mg of Sephadex DEAE A-25.

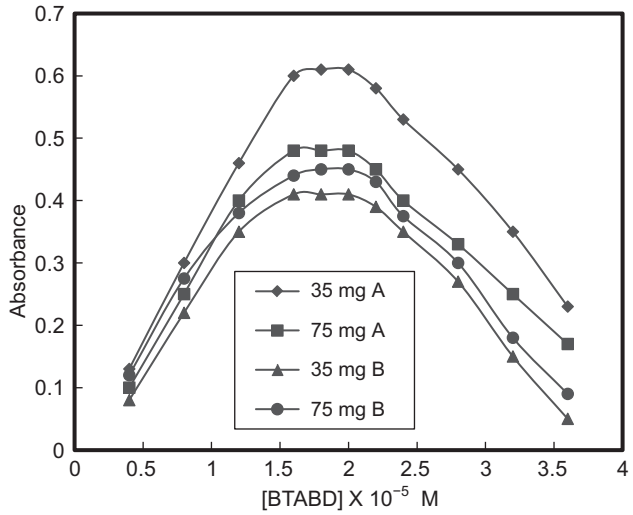

Fig. 2. Effect of BTABD concentration on the fixation and complexation of (A) 1.5 μg L^{-1} Cr(III) for 500 ml, and (B) 0.6 μg L^{-1} Cr(III) for 1000 ml; using 35 or 75 mg of Sephadex DEAE A-25.

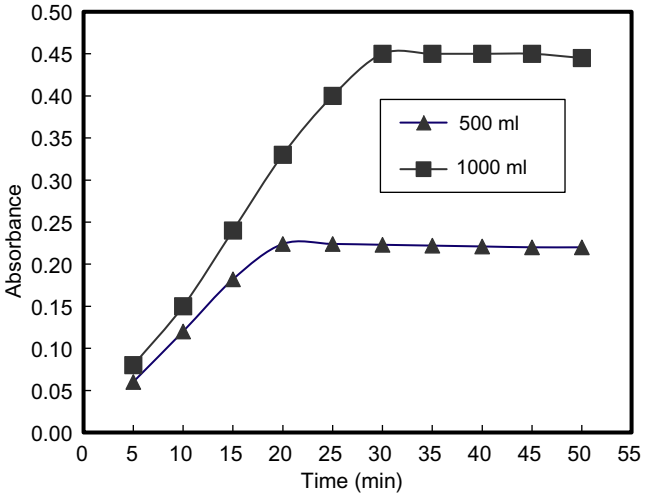

Fig. 3. Absorbance dependence on stirring time, conditions, 0.6 μg L^{-1} Cr(III); 1.8×10^{-5} M BTABD; pH 7.5; and 75 mg Sephadex DEAE A-25.

Nature of the fixed complex

The probable nature of the fixed species on Sephadex DEAE A-25 was established at a working pH of 7.5 using log–log plots (Fig. 4). The plot of the logarithm of the distribution ratio determined by batch operation [25] versus the logarithm of the BTABD concentration gave a slope of 1.0 (correlation coefficient $r = 0.9992$), indicating a BTABD to Cr(III) ratio of 1:1 in the sorbed species, which was confirmed using a fixed BTABD concentration gave a slope of 0.99 ($r = 0.9988$) indicating a BTABD to Cr(III) ratio of 1:1 in the sorbed species.

Analytical data

The calibration graphs were linear for the concentration ranges 0.05–2.4 or 0.10–4.0 μg L^{-1} of Cr(III) with r^2 of 0.9975 and 0.9994 using 35 or 75 mg of the exchanger, respectively, for the 500 ml sample system. On the other hand, for the 1000 ml sample system 0.05–1.45 μg L^{-1} with r^2 of 0.9988 using 75 mg of exchanger and 0.03–0.70 μg L^{-1} with r^2 of 0.9992 using 35 mg of that exchanger

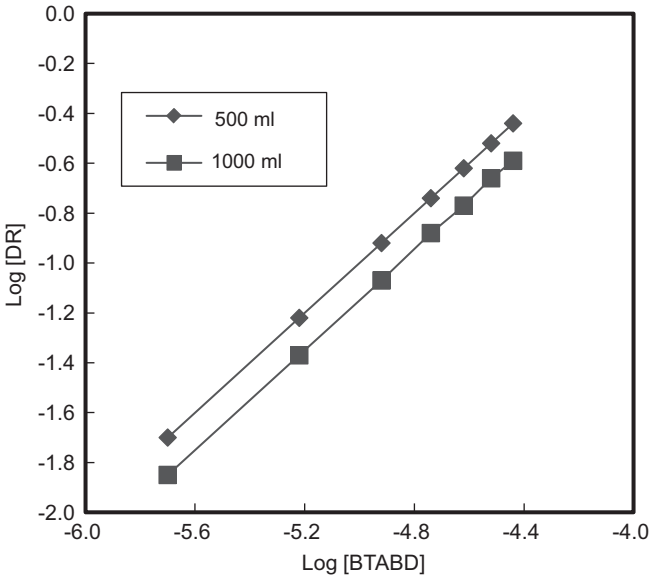

Fig. 4. The log–log plot of the distribution ratio vs. BTABD concentration; conditions, pH 7.5, 0.6 μg L^{-1} Cr(III), 75 μg Sephadex DEAE A-25, stirring time 20 and 30 min for 500 and 1000 ml samples, respectively.

were obtained. The analytical parameters (molar absorptivity, Sandell sensitivity, and Ringbom optimum concentration range) are shown in Table 1.

Reproducibility was measured for a series of eight independent determinations containing 2.0 μg L^{-1} of Cr(III) for 500 ml samples using 35 and 75 mg of the exchanger. The RSDs were 1.75 and 1.60, respectively. For 1000 ml sample, RSDs were 1.80% and 1.35% for 0.5 and 1.0 μg L^{-1} using 35 and 75 mg of that exchanger, respectively.

The sensitivity expressed as a molar absorptivity, of the proposed method was compared in Table 2 with those of the published spectrophotometric methods. The higher sensitivity of the proposed method was notable, and even greater than that of the all methods by at least 100 times, [26–31] in addition to there are no interferences from any examined anions and cations. The previously published spectrophotometric methods for chromium determination (Table 2), [26–31] have a series of limitations and they are not always suitable for the analytical practice. The disadvantages of these methods are the following: the molar absorptivity of these methods, are rather low 0.014–3.6×10^5 L mol^{-1} cm^{-1}. Comparative data from some recent studies on Cr(III) and Cr(VI) speciation are given Table 3. The proposed procedure was comparable for the procedure in the literature [5,6,9,10,32,4,33–41] with higher quantitative recovery values and lower detection limit for chromium speciation. The developed method is more sensitive in detecting chromium(VI) at ng L^{-1} levels.

One of the main advantages of SPS method is that the sensitivity can be enhanced in proportion to the volume of the sample to be analyzed. The increase in the sensitivity can be calculated from the slopes of the calibration graphs. The calculated value of the slopes of the sensitivity ratio for the sample sizes used is $S1000$: $S500 = 1.68$ by using 35 mg of exchanger and 2.34 by using 75 mg of that exchanger.

The standard deviations (s) of A_{blank}, the background absorbance measured for the blank, calculated as the average of 10 determinations and expressed as s units, for 500 and 1000 ml samples were 0.008 and 0.006, respectively. The IUPAC detection limit ($K = 3$) [42] and the quantification limit ($K = 10$) [43] were calculated for 500 and 1000 ml sample systems (Table 1). We wish to emphasize that by using 35 mg of exchanger for 1000 ml sample system

Table 1
Analytical parameters.

Parameters	Sample volume (ml)			
	500		1000	
Amount of exchanger (mg)	35	75	35	75
pH	7.5	7.5	7.5	7.5
Optimum [BATBD] (M)	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}
Stirring time (min)	20	20	30	30
Beer's range ($\mu g\ L^{-1}$)	0.05–2.4	0.10–4.0	0.03–0.70	0.05–1.45
Ringbom range ($\mu g\ L^{-1}$)	0.15–2.15	0.25–3.75	0.1–0.55	0.10–1.30
Molar absorptivity ($L\ mol^{-1}\ cm^{-1}$)	2.11×10^{7}	1.66×10^{7}	3.55×10^{7}	3.90×10^{7}
Sandell sensitivity ($ng\ cm^{-2}$)	2.46	3.13	1.46	1.33
Intercept	0.006	−0.0045	−0.007	0.003
Slope ($\mu g\ L^{-1}$)	0.41	0.32	0.68	0.75
Linear dynamic range ($\mu g\ L^{-1}$)	0.05–2.40	0.10–4.0	0.03–0.70	0.05–1.45
Correlation coefficient (r)	0.9975	0.9994	0.9992	0.9988
RSD[a] (%)	1.75	1.60	1.80	1.35
Detection limits ($ng\ L^{-1}$)	13	29	8	14
Quantification limits ($ng\ L^{-1}$)	44	95	27	47

[a] RSD is the relative standard deviations.

Table 2
The spectrophotometric methods for the chromium determination.

Reagent	Organic phase	λ_{max} (nm)	$\varepsilon \times 10^5$ ($L\ mol^{-1}\ cm^{-1}$)	Interference	Ref.
Diphenylcarbazid	—	546	0.417	Fe(III), Mo(VI), V(V), Cu(I), Hg(II)	[26]
Pentamethylen-bis (triphenylphosphonium)	Dichlorethane	365	0.014	W(VI), Mo(VI), Mn(II), ClO_4^-	[27]
Iodnitrotetrazolium chloride	1,2-Dichlorethane	250	0.88	Hg(II)	[28]
Tetrazol violet	1,2-Dichlorethane	230	1.22	Hg(II)	[28]
Nitrobluetetrazolon chloride	1,2-Dichlorethane	260	0.82	Hg(II)	[29]
Cyanine dyes	—	560	3.6	Tl(III), Sb(V), Hg(II), Re(VII), Au(III), Cu(I)	[30]
3,4-Dihydroxybenzaldehyde isonicotinoylhydrazone	pH 5.5	400	0.135	Cu(II)	[31]
BATBD-SPS (500 ml)[a]	pH 7.5	628	211		This work
BATBD-SPS (500 ml)[b]	pH 7.5	628	166		This work
BATBD-SPS (1000 ml)[a]	pH 7.5	628	355		This work
BATBD-SPS (1000 ml)[b]	pH 7.5	628	390		This work

[a] Using 35 mg of exchanger.
[b] Using 75 mg of exchanger.

Table 3
Comparative data from some recent studies on Cr(III) and Cr(VI) speciation.

Technique	Method	Detection system	DL ($\mu g\ L^{-1}$)	Ref.
Coprecipitation	Cr(VI)–ethyl xanthate complex	FAAS	0.50	[5]
SPE	*Sacchromyces cervisae*/sepiolite	FAAS	94	[6]
CPE	Cr(III)–bis(2-methoxybenzaldehyde) ethylene diimine and reduction of Cr(VI)	FAAS	0.17	[9]
SPE	Cr(VI)–cetyltrimethyl ammonium bromide	FAAS	15–20	[10]
CPE	Cr(III)–1-phenyl-3-methyl-4-benzoyl- pyrazol-5-one and reduction of Cr(VI)	ICP-AES	0.81	[32]
CPE	Cr(III)–*N*,*N*_-bis-(α-methyl salicylidene) propane-1,3-diimine and reduction of Cr(VI)	FAAS	0.10	[4]
SPE	Cr(III)–1,1,1-trifluoroacetylacetone and reduction of Cr(VI)	GC	2.0	[33]
SPE	Cr(VI)–ADPC and GFAAS	GFAAS	0.30	[34]
SPE	Cr(III) and Cr(VI)—APDC	HPLC-UV detection	0.20	[35]
SPE	Chromosorb-108/dithizone	FAAS	0.75	[36]
Solvent extraction	Cr(VI)–DPC and oxidation of Cr(III)	Spectrophotometry	2.22	[37]
SPE	Ambersorb-563/1,5 diphenyl carbazide	Spectrophotometry	3.40	[38]
SPE	Chitin/1,5-diphenyl carbazide	Spectrophotometry	50	[39]
SPE	Alumina/CTABr	Spectrophotometry	5.0	[40]
SPE	Acid activated montmorillonite–silica gel/diphenyl carbazide	Spectrophotometry	6.0	[41]
SPE	BATND-SPS (500 ml using 35 mg)	Spectrophotometry	1.3×10^{-3}	This work
SPE	BATND-SPS (500 ml using 75 mg)	Spectrophotometry	2.9×10^{-3}	This work
SPE	BATND-SPS (1000 ml using 35 mg)	Spectrophotometry	0.8×10^{-3}	This work
SPE	BATND-SPS (1000 ml using 75 mg)	Spectrophotometry	1.4×10^{-3}	This work

better values were obtained for the detection and quantification limits (s for the background absorbance of the blank was 0.0034), 0.008 and 0.027 $\mu g\ L^{-1}$, respectively. On the other hand to emphasize that by using 75 mg of that exchanger for 500 ml sample system best values were calculated and found to be 0.029 and 0.095 $\mu g\ L^{-1}$, for detection and quantification limits, respectively.

Table 4
Influences of some ions on the recoveries of 0.60 μg L^{-1} Cr(III) (N = 5, sample volume: 1000 ml).

Ions	Added as	Concentration (mg L^{-1})	Recovery of Cr^{3+} (%)[a]
K^+	KCl	10,000	98.20 ± 0.75
Na^+	NaCl	8000	99.25 ± 0.90
Mg^{2+}	$MgCl_2$	7500	100.67 ± 0.81
Ca^{2+}	$CaCl_2$	6000	101.00 ± 0.85
Cl^-	NaCl	6000	100.33 ± 1.00
SO_4^{2-}	Na_2SO_4	5000	99.00 ± 1.01
PO_4^{3-}	Na_3PO_4	4500	101.50 ± 0.96
NO_3^-	KNO_3	4000	98.67 ± 0.77
F^-	NaF	3000	102.00 ± 0.69
Borate	Na borate	2500	100.67 ± 0.95
Succinate	Na succinate	2000	99.50 ± 1.07
Ag^+	$AgNO_3$	1250	99.25 ± 0.88
Cu^{2+}	$CuSO_4$	800	98.76 ± 1.10
Ni^{2+}	$NiSO_4$	650	101.33 ± 0.80
Cd^{2+}	$Cd(NO_3)_2$	600	100.67 ± 1.15
Al^{3+}	$Al_2(SO_4)_3$	500	98.67 ± 0.93
Fe^{3+}	$FeCl_3$	350	99.00 ± 0.81
Mn^{2+}	$MnSO_4$	250	101.50 ± 1.09
Co^{2+}	$CoSO_4$	200	101.00 ± 0.84
Zn^{2+}	$ZnSO_4$	150	98.50 ± 0.69
Pb^{2+}	$Pb(NO_3)_2$	120	98.25 ± 1.05
Cr^{6+}	$K_2Cr_2O_7$	100	98.00 ± 0.86

[a]Mean ± standard deviation.

Effects of foreign ions

Various salts and metal ions were added individually to a solution containing Cr(III) and the proposed procedure was applied. The tolerance limit was set, as the diverse ion amount require causing ±3.0% error in the determination. The results obtained are given in Table 4. Under these optimized conditions, most of the probable concomitant cations and anions do not interfere. The tolerable levels of some heavy metal ions were suitable for the separation and preconcentration of the analyte ions in the real samples examined, because of the levels of transition metals in these samples were lower than their interference level.

The influences of Cr(VI) as concomitant ion were also investigated. As can be seen in Table 4, the recoveries of Cr(III) were not influenced till 100 mg L^{-1} of Cr(VI).

Determination of total chromium

In order to determine total chromium, model solutions that contain different amounts of Cr(VI) and Cr(III) were prepared. Then reduction of Cr(VI) ions to Cr(III) in the model solutions were performed using the procedure given by Bag et al. [6]. Then the procedure presented was applied to these solutions. The results are given in Table 5. The results showed that the proposed method could be applied for the determination of total chromium.

Applications

The method was applied to the speciation of Cr(III) from Cr(VI) in natural water samples for a tap water from Benha City, a Nile river water from Shobra Al-Keima and a sea water sample from Raas el-Bare. Chromium species were also spiked to these samples. The results are given in Table 6. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. The method could be applied successfully for the separation, preconcentration and speciation of trace amounts of chromium in both spiked and water samples. The relative standard deviations for water samples for Cr(III) and Cr(VI) were in the range of 1.4–3.8% and 1.2–3.5%, respectively.

Also the application of the proposed procedure for total chromium was performed to the microwave digested samples given in Table 7. The relative standard deviations for solid samples were in the range of 1.98–3.27%.

The performance of the proposed method was assessed by calculation of the t-test (for accuracy) and F-value (for precision) compared with ET AAS method. The mean values were obtained in a Student's t- and F-tests and 95% confidence limits for four degrees of freedom [44]. The results showed that the calculated values (Table 7) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consumption, shows the advantages of the proposed method over other methods. Also, there is no need for extraction or heating in the present method.

Table 5
Determination of total chromium in spiked test solutions (N = 5).

Method	Added (μg L^{-1})		Found (μg L^{-1})			Recovery (%)		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total chromium	Cr(III)	Cr(VI)	Total chromium
35 mg resin for 500 ml	0.00	2.00	0.00	1.98	1.98	–	99.00	99.00
	0.50	1.50	0.49	1.52	2.01	98.00	101.33	100.50
	1.00	1.00	1.01	1.01	2.02	101.00	101.00	101.00
	1.50	0.50	1.48	0.49	1.97	98.67	98.00	98.50
	2.00	0.00	2.01	0.00	2.01	100.50	–	100.50
75 mg resin for 500 ml	0.00	3.00	0.00	2.98	2.98	–	99.33	99.33
	0.75	2.25	0.76	2.25	3.01	101.33	100.00	100.33
	1.50	1.50	1.48	1.51	2.99	98.67	100.66	99.67
	2.25	0.75	2.27	0.76	3.03	100.89	101.33	101.00
	3.00	0.00	2.99	0.00	2.99	99.67	–	99.67
35 mg resin for 1000 ml	0.00	0.60	0.00	0.61	0.61	–	101.67	101.67
	0.15	0.45	0.15	0.44	0.59	101.33	98.22	99.00
	0.30	0.30	0.31	0.30	0.61	101.67	100.33	101.00
	0.45	0.15	0.44	0.15	0.59	98.67	100.00	99.00
	0.60	0.00	0.61	0.00	0.61	101.67	–	101.67
75 mg resin for 1000 ml	0.00	1.20	0.00	1.19	1.19	–	99.17	99.17
	0.30	0.90	0.30	0.89	1.19	98.33	98.88	98.75
	0.60	0.60	0.59	0.62	1.21	98.33	103.33	100.83
	0.90	0.30	0.91	0.30	0.91	101.11	99.00	100.78
	1.20	0.00	1.22	0.00	1.22	101.67	–	101.67

Table 6
Determination Cr(III), Cr(VI) and total chromium in some natural water samples ($N = 5$).

Samples	Added ($\mu g\ L^{-1}$)		Found ($\mu g\ L^{-1}$)			Recovery (%)		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total chromium	Cr(III)	Cr(VI)	Total Chromium
Tap water from Benha City, Egypt	–	–	0.22	0.40	0.62	–	–	–
	0.3	0.5	0.52	0.91	1.43	100.38	101.11	100.85
	0.5	0.30	0.72	0.70	1.42	100.00	99.29	99.65
	0.4	0.4	0.62	0.81	1.43	99.35	101.25	100.42
River water from Shobra Al Keima, Egypt	–	–	0.43	0.88	1.31	–	–	–
	0.5	0.75	0.93	1.63	2.55	99.46	99.82	99.69
	0.75	0.50	1.17	1.37	2.54	99.15	99.28	99.22
	0.6	0.6	1.02	1.48	2.50	99.03	100.00	99.60
Sea water from Raas El Bare, Egypt	–	–	0.51	1.13	1.64	–	–	–
	0.30	0.20	0.82	1.33	2.15	100.99	100.23	100.51
	0.25	0.25	0.76	1.37	2.13	99.34	99.28	99.30
	0.20	0.30	0.72	1.43	2.15	100.99	100.21	100.47

Table 7
The level of total chromium in some real samples after application of the proposed and AAS procedures ($N = 6$).

Sample	Concentration ($\mu g\ g^{-1}$)[a]	RSD (%)	t-test[b]	F-value[b]	ET AAS ($\mu g\ g^{-1}$)
Tobacco	1.46 ± 1.18	2.74	1.34	2.87	1.45 ± 1.66
Coffee	0.25 ± 1.35	3.15	1.58	3.21	0.26 ± 1.87
Red tea	0.18 ± 1.07	2.48	1.21	2.58	0.18 ± 1.34
Green tea	0.15 ± 1.43	3.27	1.77	3.43	0.16 ± 1.98
Soil from Benha City	24.7 ± 0.83	1.98	0.84	2.46	24.5 ± 1.21

[a] Mean ± standard deviation.
[b] Theoretical value for t- and F-values for five degrees of freedom and 95% confidence limits are 2.57 and 5.05, respectively.

Conclusion

Chromium can be determined efficiently with BTABD using SPS. The proposed method has several advantages to warrant its use:

1. The reagent is easily obtained which constitutes an advantage over the previously used group of reagents.
2. A large amount of cations and anions in the sample solution does not interfere; which is a considerable advantage over other methods.
3. The measurements can be carried out rapidly in an aqueous solution without heating, extraction or pretreatment of samples.
4. Measurements of the molar absorptivity proved it to be the more sensitive than previous reagents.

The proposed method has been applied to determine chromium in natural waters and total chromium preconcentration in microwave digested tobacco, coffee, tea, and soil samples with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

We wish to emphasize that the proposed method, as is usual in SPS methods, allow "made-to-measure" methods to be created either by selecting the sample volume or by using different amounts of exchanger.

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